Inorg. Chem. **2004**, *43*, 8387–8393

Inorganic Chemistry
Article

A Heterobimetallic Ruthenium(II)–Copper(II) Donor–Acceptor Complex as a Chemodosimetric Ensemble for Selective Cyanide Detection

Cheuk-Fai Chow,[†] Michael H. W. Lam,*,[†] and Wai-Yeung Wong[‡]

*Department of Biology & Chemistry, City University of Hong Kong, 83 Tat Chee Avenue,
Hong Kong SAR, China, and Department of Chemistry, Hong Kong Baptist University,
Waterloo Road, Kowloon Tong, Hong Kong SAR, China*

Received June 7, 2004

A trinuclear heterobimetallic Ru(II)–Cu(II) donor–acceptor complex, $\{Ru^{II}({}^tBubpy)(CN)_4–[Cu^{II}(dien)]_2\}(ClO_4)_2$ (^{t}Bubpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine; dien = diethylenetriamine) (**1**), has been synthesized and successfully used as an chemodosimetric ensemble for the specific detection of cyanide in aqueous DMF. X-ray crystallography, solid and solution IR spectroscopy, and conductivity measurements reveal that complex **1** is a one-dimensional polymer in the crystalline state and dissociates into its $\{Ru^{II}({}^tBubpy)(CN)_2[(CN)Cu^{II}(dien)L]_2\}^{2+}$ (L = solvent) monomeric units in polar solvents. The MLCT transition and luminescence properties of the solvatochromic $[Ru^{II}({}^tBubpy)(CN)_4]^{2-}$ donor are perturbed by the coordination of two Cu(II) acceptors but restored in the presence of CN^-. Spectroscopic and mass spectrometric studies confirm the cleavage of the cyano bridge between Ru(II) and Cu(II) of the chemodosimetric ensemble after the binding of cyanide to the Cu(II) centers. The overall binding constant, K_B, between **1** and CN^- is measured to be $(7.39 \pm 0.23) \times 10^6\ M^{-2}$. A detection limit of 1.2 μM (0.03 ppm) of CN^- in aqueous DMF (pH 7.4) is achievable. Thermodynamic evaluation shows that the analyte specificity of chemodosimeter **1** is attributable to the relative stability of the donor–acceptor complex to that of adducts formed between the acceptor metal center and the analytes.

Introduction

Development of new optical molecular dosimeters/sensors for environmentally important anions is an emerging field.[1] Classical molecular chemosensors are, in general, molecular assemblies of molecular recognition (receptor) units and signal transduction units where sensing responses are triggered by the receptor−analyte interaction.[2] However, the requirement for the receptor−analyte binding events to trigger signal transduction has posed considerable constraints on their design and synthesis. Recently, a new chemosensing scheme has emerged which allows greater flexibility to the molecular design of chemosensors. Such a competitive displacement approach resembles antibody-based immunoassays in that target analytes have to compete for specific molecular receptors with fluorogenic/chromogenic signaling analogues.[3] We have explored the feasibility of using heterobimetallic donor−acceptor coordination complexes as chemodosimetric ensembles and reported a cyano-bridged heterobimetallic Ru(II)−Pt(II) complex that produces specific luminescent responses to sulfhydryl-containing amino acids and peptides in aqueous media.[4] With suitable donor−

---

* Author to whom correspondence should be addressed. E-mail: bhmhwlam@cityu.edu.hk. Phone: (852)-2788-7329. Fax: (852)-2788-7406.

[†] City University of Hong Kong.

[‡] Hong Kong Baptist University.

(1) (a) Schmidtchen, F. P.; Berger, M. *Chem. Rev.* **1997**, *97*, 1609. (b) Gale, P. A. *Coord. Chem. Rev.* **2000**, *199*, 181. (c) Gale, P. A. *Coord. Chem. Rev.* **2001**, *199*, 79. (d) Best, M. D.; Tobey, S. L.; Anslyn E. V. *Coord. Chem. Rev.* **2003**, *240*, 3.

(2) (a) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515. (b) Schmidtchen, F. P.; Berger, M. *Chem. Rev.* **1997**, *97*, 1609.

(3) (a) Metzger, A.; Anslyn, E. V. *Angew Chem., Int. Ed.* **1998**, *37*, 649. (b) Nikura, K.; Metzger, A.; Anslyn, E. V. *J. Am. Chem. Soc.* **1998**, *120*, 8533. (c) Lavigne, J. J.; Anslyn, E. V. *Angew. Chem., Int. Ed.* **1999**, *38*, 3666. (d) Wiskur, S. L.; Anslyn, E. V. *J. Am. Chem. Soc.* **2001**, *123*, 10109. (e) Ait-Haddou, H.; Wiskur, S. L.; Lynch, V. M.; Anslyn, E. V. *J. Am. Chem. Soc.* **2001**, *123*, 11296. (f) Fabbrizzi, L.; Leone, A.; Tagliette, A. *Angew Chem., Int. Ed.* **2001**, *40*, 3066. (g) Hortalá, M. A.; Fabbrizzi, L.; Marcotte, N.; Stomeo, F.; Taglietti, A. *J. Am. Chem. Soc.* **2003**, *125*, 20. (h) McCleskey, S. C.; Griffin, M. J.; Schneider, S. E.; McDevitt, J. T.; Anslyn, E. V. *J. Am. Chem. Soc.* **2003**, *125*, 1114. (i) McCleskey, S. C.; Floriano, P. N.; Wiskur, S. L.; Anslyn, E. V.; McDevitt, J. T. *Tetrahedron* **2003**, *59*, 10089. (j) Tobey, S. L.; Anslyn, E. V. *Org. Lett.* **2003**, *5*, 2029. (k) Nguyen, B. T.; Wiskur, S. L.; Anslyn, E. V. *Org. Lett.* **2004**, *6*, 2499.

(4) Chow, C. F.; Chiu, B. K. W.; Lam, M. H. W.; Wong, W. Y. *J. Am. Chem. Soc.* **2003**, *125*, 7802.

10.1021/ic0492587 CCC: $27.50

acceptor combinations, it is envisioned that chemodosimeters with fine-tuned analyte specificity can be obtained.

Cyanide is one of the most concerned anions in the environment because of its high toxicity and its being widely used in industries. It is extraordinarily poisonous as it depresses the central nervous system by interacting strongly with the heme in cytochrome-a_3.[5] The normal fatal dose of potassium cyanide to human is 2−3.6 mg/kg, and the maximum allowed level for cyanide in drinking water is 0.2 mg/L (i.e. 0.2 ppm).[5,6] Nevertheless, it is extensively used in a large number of industrial applicants such as mining,[5a] metallurgy,[5a,7a] photographic processing,[7a] and the production of nitriles, nylon, and acrylic plastics.[7b] Many analytical techniques, such as titrimetry,[8a] spectrophotometry,[8a−c] potentiometry,[8d] chromatography,[8e] and capillary electrophoresis,[8e] have been adopted for the determination of cyanide. However, these analytical methods usually suffer from extensive procedures, a lack of specificity, and expensive instrumentation. It is surprising to realize that an example of molecular dosimeters/sensors for cyanide is scarce.[9]

In this work, the synthesis and characterization of a new Ru(II)−Cu(II) heterobimetallic donor−acceptor molecular chemodosimetric ensemble, $\{Ru^{II}(^tBubpy)(CN)_4-[Cu^{II}(dien)]_2\}(ClO_4)_2$ (^{t}Bubpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine; dien = diethylenetriamine) (**1**), is reported. The ensemble is found to produce both colorimetric and luminescent responses specifically to cyanide in aqueous DMF.

Experimental Section

Materials and Reagents. 4,4′-Di-*tert*-butyl-2,2′-bipyridine (^{t}Bubpy), 2,2′-bipyridine (bpy), diethylenetriamine (dien), *N*-(2-hydroxyethyl)piperazine-*N*′-(2-ethanesulfonic acid) (HEPES), potassium cyanide, sodium cyanide, potassium carbonate, $RuCl_3\cdot 3H_2O$, $Cu(ClO_4)_2\cdot 6H_2O$, sodium chloride, sodium nitrate, sodium thiocyanide, sodium acetate, sodium azide, sodium dihydrogen phosphate, sodium hydrogen carbonate, and sodium sulfate were obtained from Aldrich. $K_2[Ru(^tBubpy)(CN)_4]$,[10] *cis*-$[Ru(bpy)_2(CN)_2]$,[11] and $Cu[(dien)(ClO_4)](ClO_4)$[12] were synthesized according to literature methods. All solvents used were of analytical grade.

Equipment. Infrared spectra in the range 500−4000 cm^{-1} in KBr plates or in methanol were recorded on a Perkin-Elmer model FTIR-1600 spectrometer. Conductivity measurements were performed on a Cole-Parmer 01481-61 conductivity meter. UV−vis spectra were measured on a Hewlett-Packard 8452A ultraviolet visible diode array spectrophotometer. Emission spectra were recorded using a Horiba FluoroMax-3 spectrofluorometer with 5 nm slit width and 0.5 s integration time. ^{1}H NMR spectra were recorded using a Varian YH300 300 MHz NMR spectrometer. Electrospray mass spectra (ESI-MS) were measured by a PE SCIEX API 365 LC/MS/MS system. Elementary analyses were performed on a Vario EL elementary analyzer.

$\{Ru(^tBubpy)(CN)_4[Cu(dien)]_2\}(ClO_4)_2\cdot 3H_2O$ (1). A mixture of $K_2[Ru(^tBubpy)(CN)_4]$ (0.276 g, 0.5 mmol) and $[Cu(dien)(ClO_4)](ClO_4)$ (0.366 g, 1 mmol) was stirred in 10 mL of a water/methanol mixture (1:1 v/v) at room temperature for 30 min and was allowed to stand overnight. Green crystalline products were obtained by slow evaporation of solvent. Yield: 0.427 g (85%). IR (KBr): 2055 cm^{-1}, $\nu_{C\equiv N}$. ES-MS (CH_3OH, +ve mode): *m/z* 907, $[M - ClO_4]^+$. Anal. Calcd for $C_{30}Cl_2Cu_2H_{50}N_{12}O_{11}Ru$: C, 33.97; H, 5.28; N, 15.85. Found: C, 33.71; H, 5.17; N, 15.98.

In Situ Synthesis of *cis*-$[Ru(bpy)_2(CN)_2]-[Cu(dien)]^{2+}$ (2). A mixture of *cis*-$[Ru(bpy)(CN)_2]$ (0.0465 g, 0.1 mmol) and $[Cu(dien)(ClO_4)](ClO_4)$ (2.925 g, 8 mmol) was stirred in 50.0 mL of methanol at room temperature for 30 min. Due to the relatively low stability of the donor−acceptor adduct, **2** was not isolated and its methanol solution was used instead in all spectrofluorometric titrations. Stoichiometry of the adduct was determined by mole ratio plot of *cis*-$[Ru(bpy)(CN)_2]$ by $[Cu(dien)]^{2+}$ and was found to be 1:1 *cis*-$Ru(bpy)_2(CN)_2$:$[Cu(dien)]^{2+}$.[13]

Crystal Structure Determination. Crystallographic data for complex **1**, $\{Ru(^tBubpy)(CN)_4[Cu(dien)]_2\}(ClO_4)_2\cdot 3H_2O$: formula = $C_{30}H_{50}Cl_2Cu_2N_{12}O_{11}Ru$; fw = 1059.92; triclinic; space group $P1$; $a = 11.006(2)$, $b = 13.471(3)$, $c = 16.514(3)$ Å; $\alpha = 93.793(3)$, $\beta = 94.251(4)$, $\gamma = 112.956(4)°$; $V = 2236.2$ (8) Å^3, $Z = 2$; $D_c = 1.574$ mg m^{-3}; μ(Mo Kα) = 1.460 mm^{-1}; $F(000) = 1088$; $T = 273$ K. A green crystal of dimensions 0.28 × 0.18 × 0.15 mm mounted on a glass fiber was used for data collection at 0 °C on a Bruker Axs SMART 1000 CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). A total of 10 303 reflections were measured, of which 7508 were unique and R(int) = 0.0407. A total of 5218 reflections with $I > 2\alpha(I)$ were considered observed and used in the structural analysis. The collected frames were processed with the software SAINT,[14] and an absorption correct was applied (SADABS[15]) to the collected reflections. The structure of the complex was solved by direct methods (SHELXTL[16]) in conjunction with standard difference Fourier techniques and subsequently refined by full-matrix least squares on F^2. Convergence for 508 variable parameters by the least-squares refinement for 5218 reflections with $I > 2\alpha(I)$ was reached at R = 0.0723 and wR = 0.1750 with a goodness-of-fit of 0.896. The final difference Fourier map was featureless, with maximum positive and negative peaks of 1.548 and −1.240 e Å^{-3}, respectively. All non-hydrogen atoms were assigned with anisotropic displacement parameters. The hydrogen atoms were generated in their idealized positions and allowed to ride on the respective carbon atoms.

---

(5) (a) Miller, G. C.; Pritsos, C. A. *Cyanide: Soc., Ind. Econ. Aspects, Proc. Symp. Annu. Meet*. 2001, 73. (b) Vennesland, B.; Comm, E. E.; Knownles, C. J.; Westly, J.; Wissing, F. *Cyanide in biology*; Academic Press: London, 1981.

(6) The U.S. Environmental Protection Agency (EPA) has set the maximum contaminant level goals for cyanide in drinking water to 0.2 ppm.

(7) (a) Ikediobi, C. O.; Wen, L.; Latinwo, L. M. *Am. Environ. Lab*. **1997**, *9*, 20. (b) *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed.; Wiley-VCH: New York, 1999.

(8) (a) *APAH, AWWA, and WPCF, Standard Methods for the Examination of Water and Wastewater*, 17th ed.; American Public Health Association: Washington, DC, 1989. (b) Sulistyarti, H.; Cardwell, T. J.; Kolev, S. D. *Anal. Chim. Acta* **1997**, *357*, 103. (c) Kuban, V. *Anal. Chim. Acta* **1992**, *259*, 45. (d) Vallejo-Pecharromán, B.; Luque de Castro, M. D. *Analyst* **2002**, *127*, 267. (e) Aguilar, M.; Farran, A.; Marti, V. *J. Chromatogr., A* **1997**, *778*, 397.

(9) (a) Kim, Y. H.; Hong, J. I. *Chem. Commun*. **2002**, 512. (b) Anzenbacher, P.; Tyson, Jr., D. S.; Jursíková, K.; Castellano, F. N. *J. Am. Chem. Soc*. **2002**, *124*, 6232. (c) Ros-Lis, J. V.; Martínez-Máñez, R.; Soto, J. *Chem. Commun*. **2002**, 2248.

(10) (a) Krause, R. A. *Inorg. Chim. Acta* **1977**, *22*, 209. (b) Kato, M.; Yamauchi, S.; Hirota, N. *J. Phys. Chem*. **1989**, *93*, 3422.

(11) Demas, J. N.; Turner, T. F.; Crosby, G. A. *Inorg. Chem*. **1969**, *8*, 674.

(12) Trendafilova, N.; Nikolov, G. S.; Bauer, G.; Kellner, R. *Inorg. Chim. Acta* **1993**, *210*, 77.

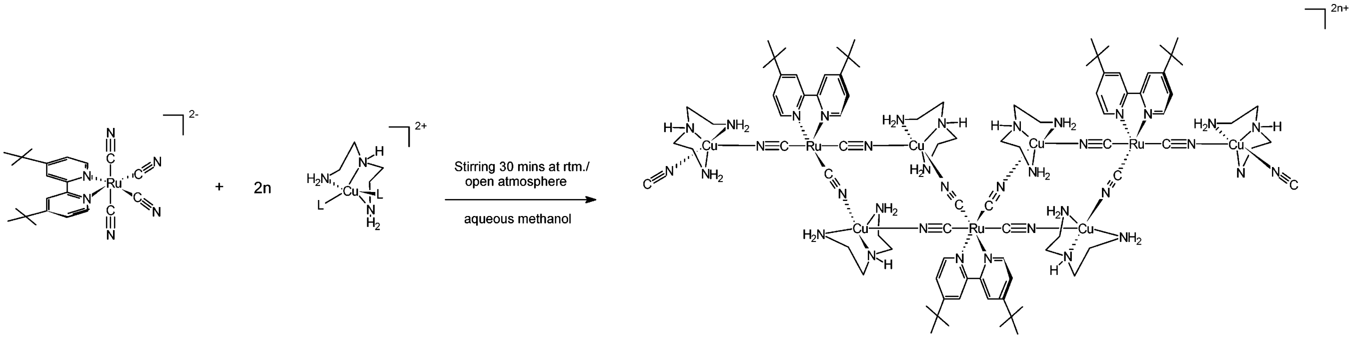
(13) Details are given in the Supporting Information.

(14) *SAINT Reference Manual*; Siemens Energy and Automation: Madison, WI, 1994−1996.

(15) Sheldrick, G. M. *SADABS, Empirical Absorption Correction Program*; University of Göttingen: Göttingen, Germany, 1997.

(16) Sheldrick, G. M. *SHELXTL Reference Manual*, version 5.1; Siemens: Madison, WI, 1997.

Scheme 1. Reaction of $[Ru(^tBubpy)(CN)_4]^{2-}$ with $Cu[(dien)]^{2+}$ in Aqueous Methanol



Spectroscopic and Spectrofluorometric Titrations. All solvents used in UV−vis spectroscopic and spectrofluorometric titrations were of analytical grade. DMF used was purified by distillation. HEPES buffer used was 10 mM at pH 7.4. For all anions, their sodium salts were used in the titrations. All the titrations were carried out in aqueous DMF (1:1 v/v) (1.50 mL of aqueous HEPES buffer at pH 7.4 + 1.50 mL of DMF). Measurements were taken after equilibrium has been acquired.

Job's Plots. A series of acceptor (i.e. $[Cu(dien)]^{2+}$) solutions were mixed with the donor (i.e. $[Ru(^tBubpy)(CN)_4]^{2-}$/*cis*-$[Ru(bpy)(CN)_2]$/anion analytes) solutions under the condition that the sum of the concentration of the donor and acceptor solutions is constant. Spectral changes (A/A_O or I/I_O) of the resulting mixtures were plotted as a function of mole fraction of the donors. All the measurements were carried out in aqueous DMF (1:1 v/v) (1.50 mL of aqueous HEPES buffer at pH 7.4 + 1.50 mL of DMF).

Determination of Binding Constants. For the determination of binding strengths of the Ru(II)−Cu(II) donor−acceptor complexes **1** and **2**, a series of the Ru(II) donor ($[Ru(^tBubpy)(CN)_4]^{2-}$ and *cis*-$[Ru(bpy)(CN)_2]$, respectively) solutions at a fixed concentration were mixed with the $[Cu(dien)]^{2+}$ acceptor solutions at various concentrations. Luminescence intensity of the resultant mixtures at 656 and 634 nm, respectively, was measured. Luminescent responses in terms of $I_O/(I - I_O)$ were plotted as a function of $[Cu(dien)]^{2+}$ concentration. For the determination of binding strengths of the various Cu(II)−anion adducts, a series of $[Cu(dien)]^{2+}$ solutions at a fixed concentration were mixed with the anion solutions at various concentrations. Absorbance of the resultant mixtures at 417 nm was measured. Spectral responses in terms of $A_O/(A - A_O)$ were plotted as a function of the anion concentration. All measurements were carried out in aqueous DMF (1:1 v/v). According to the donor−receptor binding ratio (1:1 or 1:2) determined by Job's plots, binding constants of the donor−acceptor adducts were analyzed by Benesi−Hildebrand[13,17] 1:1 or 1:2 equation, respectively. Binding constants, K_B, were estimated from the ratio between the *y*-intercept and the slope of the best straight line.

The 1:1 donor−acceptor interaction was analyzed according to Benesi−Hildebrand equations for spectroscopic UV−vis titration (eq i) or spectrofluorometric titration (eq ii).

$$\frac{A_O}{A - A_O} = \left(\frac{\epsilon_O}{\epsilon_O - \epsilon}\right)\left(\frac{1}{K_B[\text{substrate}]} + 1\right) \qquad \text{(i)}$$

$$\frac{I_O}{I - I_O} = \left(\frac{a}{b - a}\right)\left(\frac{1}{K_B[\text{substrate}]} + 1\right) \qquad \text{(ii)}$$

The 1:2 donor−acceptor interaction was analyzed according to Benesi−Hildebrand equations for spectroscopic UV−vis titration (eq iii) or spectrofluorometric titration (eq iv).

$$\frac{A_O}{A - A_O} = \left(\frac{\epsilon_O}{\epsilon_O - \epsilon}\right)^2\left(\frac{1}{K_B[\text{substrate}]^2} + 1\right) \qquad \text{(iii)}$$

$$\frac{I_O}{I - I_O} = \left(\frac{c}{d - c}\right)^2\left(\frac{1}{K_B[\text{substrate}]^2} + 1\right) \qquad \text{(iv)}$$

A_O and A are the absorbance of $[Cu(dien)]^{2+}$ in the absence and presence of the anion analytes respectively; ϵ_O and ϵ are the corresponding molar absorption coefficients of $[Cu(dien)]^{2+}$ in the absence and presence of the anion analytes, respectively. I_O and I are luminescence intensity of $[Ru(^tBubpy)(CN)_4]^{2-}$ and *cis*-$[Ru(bpy)(CN)_2]$ at 656 and 634 nm, respectively, in the absence and presence of $[Cu(dien)]^{2+}$; $a-d$ are constants. [substrate] is the concentration of the titrants. In cases of titrating of **1** with cyanide, the binding constant, K_B, represents the substrate binding strength of each Cu(II) center on the donor−acceptor Ru(II)−Cu(II). Gibbs free energy of formation of the donor−acceptor adducts ($-\Delta G$/kJ mol^{-1}) was evaluated from the corresponding binding constants as stated in eq v:[18]

$$\Delta G = -RT \ln K_B \qquad \text{(v)}$$

R is the gas constant, and T is the temperature at which the experiments were conducted.

Results and Discussion

Synthesis and Characterization. Heterobimetallic complex **1** was formed by simply stirring 2 equiv of $Cu[(dien)(ClO_4)](ClO_4)$ complex with 1 equiv of $K_2[Ru(^tBubpy)(CN)_4]$ in 1:1 ratio of water/methanol mixture in open atmosphere at room temperature (Scheme 1). It was isolated as air-stable green needle-shaped crystals in good yield. Complex **1** is soluble in polar organic solvents such as methanol, DMSO, and DMF. Besides X-ray crystallography, formation of the cyano-bridged bimetallic complex was also confirmed by IR spectroscopic studies, where $\nu_{C\equiv N}$ of $K_2[Ru(^tBubpy)(CN)_4]$ at 2042, 2057, 2073, and 2096 cm^{-1} were shifted to 2055 cm^{-1} in crystalline **1**. When complex **1** is dissolved in polar solvents, it readily dissociates into its solvated monomeric units. The IR spectrum of **1** in methanol reveals two $\nu_{C\equiv N}$ at

---

(17) *IUPAC Stability Constants Database*, version 5; IUPAC and Academic Software: Yorks, U.K., 2001.

(18) Connors, K. A. *Binding Constants, The Measurement of Molecular Complex Stability*; John Wiley and Sons: New York, 1987.

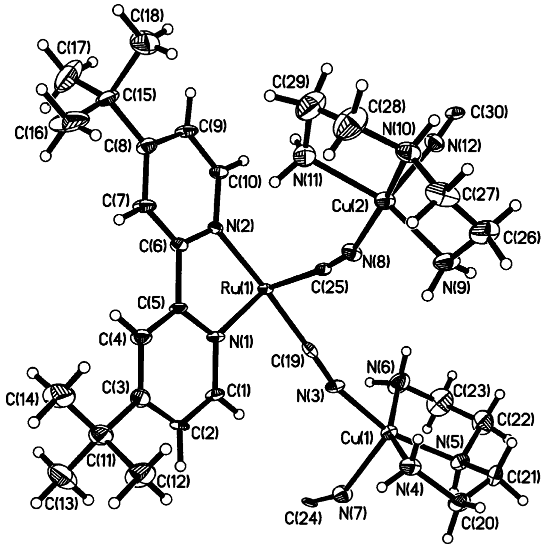


Figure 1. Perspective view of the crystallographically independent unit of **1**. Hydrogen atoms were omitted for clarity.

2059 and 2065 cm^{-1}. Conductivity measurement in DMF shows that the solvated form of **1** is an 1:2 electrolyte.

Crystal Structure Determination. Single crystals of **1** (green needles) were grown from slow evaporation of a concentrated complex in 1:1 ratio of water/methanol mixture in open atmosphere. A perspective view of the crystal structure of **1**, with atom labeling, is shown in Figure 1. The crystal structure of **1** is an one-dimensional polymer chain of $\{Ru^{II}({}^tBubpy)(CN)_2[(CN)Cu^{II}(dien)]_2\}^{2+}$ monomeric units (Figure 2). Along the polymer chain, each Cu(II) is bridged to two Ru(II) centers via cyano bridges. The coordination geometry of the Cu(II) centers is a distorted trigonal bipyrimidal via coordination to a tridentate dien ligand together with two cyano bridges. The averaged bond distance between Ru and the cyano-C is 2.009 Å, and that between Cu and cyano-N is 2.061 Å. The mean bond distance between Cu and the dien-N is 2.034 Å. The two Ru−C≡N−Cu bridges are slightly bent from linearity with the mean bond angles of 175.78° at Ru−C≡N and 161.4° at C≡N−Cu. Crystal data and other X-ray crystallographically experimental details are summarized in Table 1. Selected bond distances and angles are summarized in Table 2.

Table 1. Crystallographic Data for $\{Ru({}^tBubpy)(CN)_4[Cu(dien)]_2\}(ClO_4)_2{\cdot}3H_2O$ (**1**)

empirical formula	$C_{30}H_{50}Cl_2Cu_2N_{12}O_8Ru{\cdot}3H_2O$
fw	1059.92
temp, K	273
wavelength, Å	0.710 73
cryst system	triclinic
space group	$P\bar{1}$
a, Å	11.006(2)
b, Å	13.471(3)
C, Å	16.514(3)
α, deg	93.792(3)
β, deg	94.251(4)
γ, deg	112.956(4)
V, Å^3	*2236.2(8)*
Z	2
d(calcd), Mg m^{-3}	1.574
abs coeff, mm^{-1}	1.460
F(000)	1088
cryst dimens, mm	0.28 × 0.18 × 0.15
θ range for data collcn, deg	1.96−25.00
limiting indices	*h*, −13 to 12; *k*, −16 to 13; *l*, −19 to 19
reflcns collcd	10 303
unique reflcns	7508
R_{int}	0.0407
obsd reflcns [$I > 2\alpha(I)$]	5218
completeness to $\theta = 25.00°$, %	95.3
max and min transm	1.0000, 0.6849
data/restraints/params	7508/0/508
goodness of fit on F^2	0.896
final R indices [$I > 2\alpha(I)$]	R1 = 0.0723, wR2 = 0.1750
R indices (all data)	R1 = 0.1060, wR2 = 0.1959
largest diff peak and hole, e Å^{-3}	1.548, −1.240

Electronic Absorption and Luminescent Properties. A low-energy absorption band at ca. 375−500 nm and emission band at ca. 550−750 nm dominate the electronic absorption and emission spectra of $K_2[Ru({}^tBubpy)(CN)_4]$ and complex **1**. With reference to previous spectroscopic works, the low-energy absorption band is attributable to the Ru (d*π*) → ^{t}-Bubpy (*π**) MLCT absorption, while the low-energy emission band is assigned as a ^{t}Bubpy (*π**) → Ru (d*π*) ^{3}MLCT

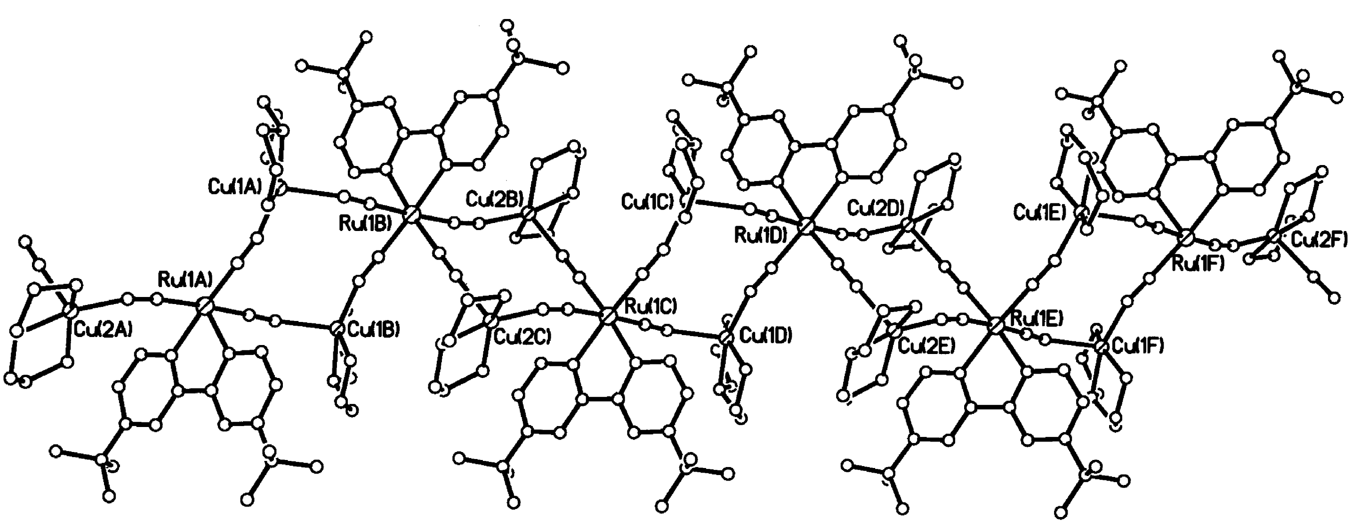


Figure 2. Perspective view of a fragment of the one-dimensional chain of $Ru({}^tBubpy)(CN)_4[Cu(dien)]_2(ClO_4)_2{\cdot}3H_2O$ (**1**) along the *b* axis. The crystallization water molecules, hydrogen atoms, and perchlorate anions were omitted for clarity.

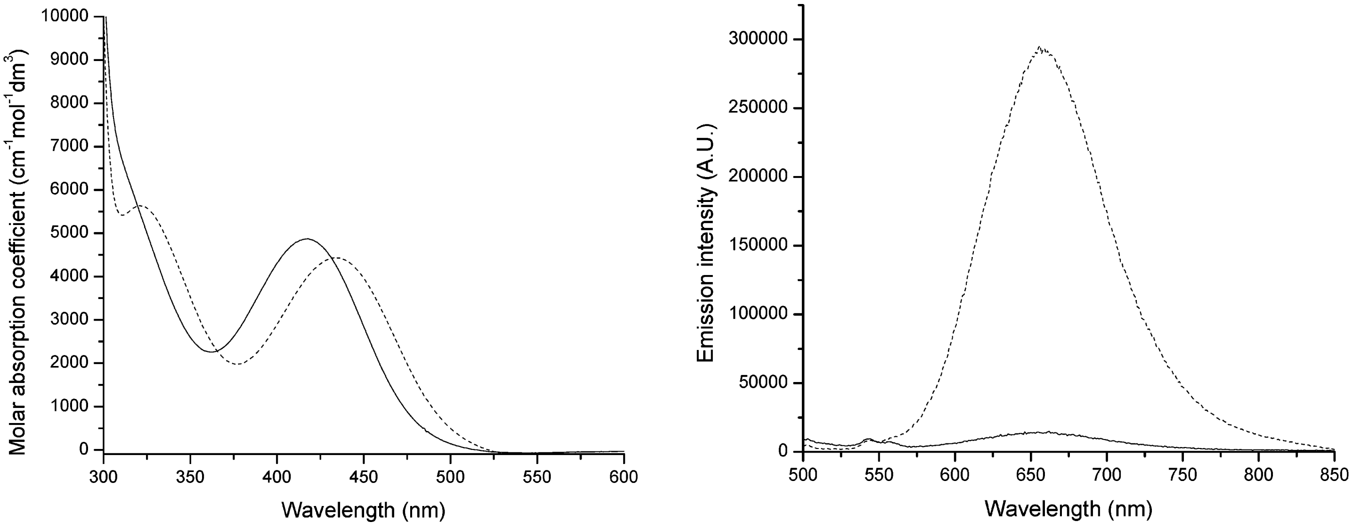


Figure 3. Absorption (left) and luminescent (right) spectra of $K_2Ru(^tBubpy)(CN)_4$ (---) and **1** (—) in aqueous DMF (1:1 v/v) (1.50 mL of aqueous HEPES buffer at pH 7 + 1.50 mL of DMF) at 298 K. Luminescent spectra were obtained with 467 nm excitation.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of $\{Ru(^tBubpy)(CN)_4[Cu(dien)]_2\}(ClO_4)_2\cdot 3H_2O$ (**1**)

Bond Lengths			
Ru(1)−N(1)	2.100(6)	Cu(1)−N(3)	1.951(7)
Ru(1)−N(2)	2.115(6)	Cu(1)−N(4)	2.002(8)
Ru(1)−C(19)	1.973(9)	Cu(1)−N(5)	2.040(7)
Ru(1)−C(25)	2.058(9)	Cu(1)−N(6)	2.030(9)
Ru(1)$^{\#1}$−C(24)	2.023(8)	Cu(1)−N(7)	2.166(7)
Ru(1)$^{\#2}$−C(30)	1.983(9)	Cu(2)−N(8)	1.953(7)
C(19)−N(3)	1.179(11)	Cu(2)−N(9)	2.048(8)
C(24)−N(7)	1.180(10)	Cu(2)−N(10)	2.025(8)
C(25)−N(8)	1.140(11)	Cu(2)−N(11)	2.059(8)
C(30)−N(12)	1.175(11)	Cu(2)−N(12)	2.177(7)
Bond Angles			
C(19)−Ru(1)−C(25)	92.5(3)	Ru(1)$^{\#1}$−C(24)−N(7)	176.0(7)
C(19)−Ru(1)−C(24)$^{\#1}$	90.0(3)	Ru(1)$^{\#2}$−C(30)−N(12)	178.6(7)
C(19)−Ru(1)−C(30)$^{\#2}$	90.0(3)	N(3)−Cu(1)−N(7)	103.0(3)
C(24)$^{\#1}$−Ru(1)−C(25)	177.4(3)	N(8)−Cu(2)−N(12)	98.3(3)
C(30)$^{\#2}$−Ru(1)−C(25)	89.8(3)	Cu(1)−N(3)−C(19)	165.8(7)
C(30)$^{\#2}$−Ru(1)−C(24)$^{\#1}$	89.2(3)	Cu(1)−N(7)−C(24)	145.4(7)
Ru(1)−C(19)−N(3)	177.3(7)	Cu(2)−N(8)−C(25)	161.5(7)
Ru(1)−C(25)−N(8)	171.2(7)	Cu(2)−N(12)−C(30)	172.9(7)

emission.[19] Figure 3 shows the MLCT absorption and ^{3}MLCT emission of the $K_2[Ru(^tBubpy)(CN)_4]$ system before and after bridging by the $[Cu(dien)]^{2+}$ acceptors. The aqueous DMF solution of $K_2[Ru(^tBubpy)(CN)_4]$ is orange in color and gives strong phosphorescence at λ_{max} 656 nm, while that of complex **1** is green in color with very weak phosphorescence. Upon coordination of the $[Cu(dien)]^{2+}$ acceptor, the MLCT transition of the Ru(II)−diimine chromophore shifts from 433 to 417 nm and the ^{3}MLCT emission shifts from 656 to 646 nm with a drastic reduction in luminescent intensity. The concomitant blue-shift in both of the MLCT electronic transition and ^{3}MLCT emission is understandable in terms of the electron-withdrawing effect of the $[Cu(dien)]^{2+}$ acceptor on stabilizing the d-orbitals of the Ru(II)−diimine chromophore. The effect is consistent with those observed in a number of related solventochromic systems in which protons,[20] boron halides,[21] and transition-metal ions[22,23] act as Lewic acids. The decrease in ^{3}MLCT emission intensity of **1** is the consequence of coordination of the diamagnetic Cu(II) complexes to the Ru(II)−diimine chromophore.[24]

Binding Properties of Chemodosimeter 1 with Common Anions. Addition of cyanide into an aqueous DMF solution of **1** at pH 7.4 restores the characteristic spectroscopic properties of $[Ru(^tBubpy)(CN)_4]^{2-}$. Figure 4 shows the colorimetric and luminescent responses of **1** to cyanide and other common anions (SO_4^{2-}, HCO_3^-, HPO_4^{2-}, N_3^-, CH_3COO^-, NCS^-, NO_3^-, and Cl^-) in aqueous DMF at pH 7.4. The green to orange colorimetric responses induced by CN^- is due to the red-shift of the absorption band from 417 to 433 nm. The intense red color emission is resulted from the shift of the emission maxima from 646 to 656 nm with a significant enhancement in luminescent intensity.

Job's plot of the luminescent responses of **1** to CN^- reveals that the maximum response occurs at **1**:CN^- mole ratio of 1:4.[13] Thus, each Cu(II) center in **1** binds two cyanide anions. The production of the dual luminescent/colorimetric responses of **1** to cyanide is attributable to the coordination of CN^- to the Cu(II) centers of **1**, causing the cleavage of the cyano-bridged donor−acceptor complex. The close resemblance of the colorimetric and luminescent responses to the MLCT characteristics of $[Ru(^tBubpy)(CN)_4]^{2-}$ and the subsequent observation of the $[Ru^{II}(^tBubpy)(CN)_4 + Na]^-$ (m/z 497, $[M + Na]^-$) in the ES-MS[13] of the **1** + NaCN mixture suggest that the cyano bridges between Ru(II) and Cu(II) of the trinuclear complex are cleaved after the binding of cyanide to the Cu(II) centers of **1**. Ligand-field transitions of the resulting Cu(II)−bis(cyano) complex do not contribute much to the colorimetric responses as they are masked by the allowed MLCT transition of $[Ru(^tBubpy)(CN)_4]^{2-}$. Fitting of the luminescent responses to the 1:2 binding model yields the overall binding constant, K_B, of $(7.39 \pm 0.23) \times 10^6$ M^{-2} between **1** and CN^-.[13] The sensitivity of the chemodosimeter for CN^- in the luminescent mode of detection (as 3:1 signal:noise ratio) can reach 1.2 μM (0.03 ppm) in water

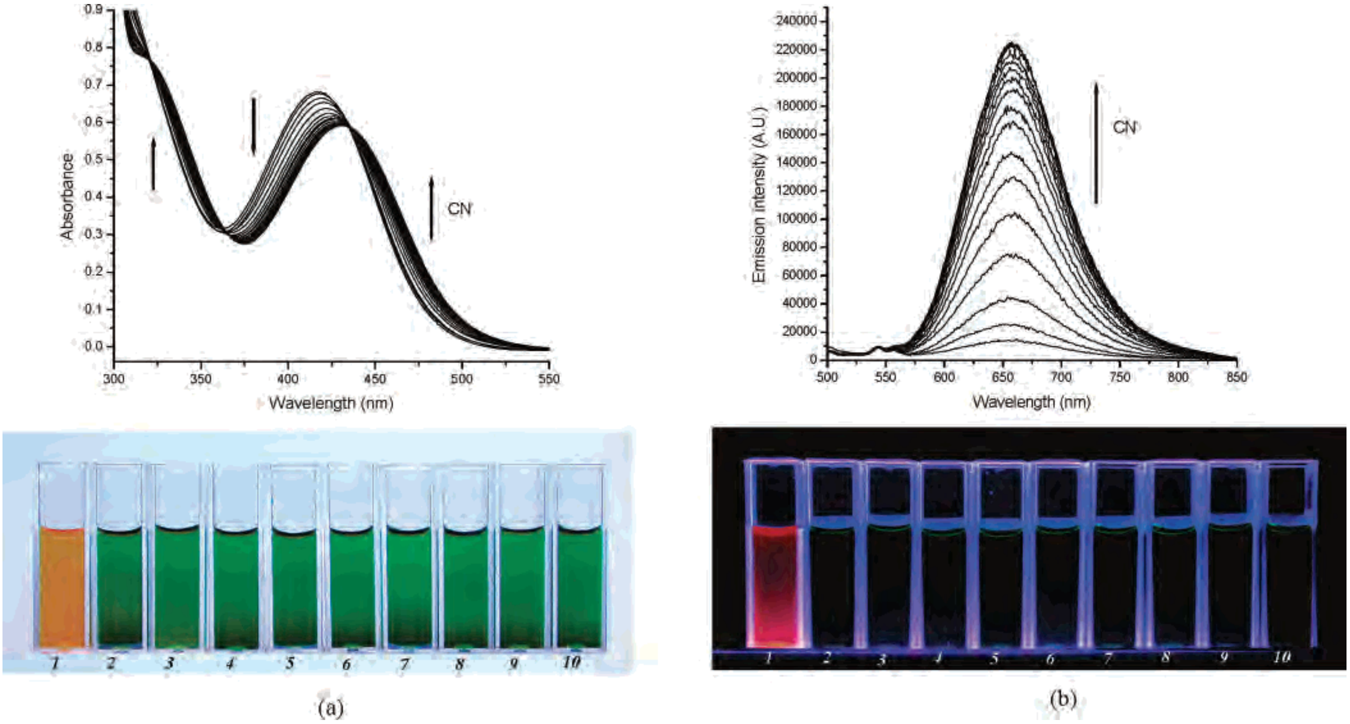


Figure 4. Spectroscopic responses of solvated **1** in aqueous DMF (1:1 v/v) (pH 7.4) toward CN^-: (a) UV−vis spectroscopic titration; (b) spectrofluorimeric titration of **1** (1.40×10^{-4} M) by sodium cyanide (0 to 1.12×10^{-3} M). Emission spectra were obtained with 467 nm excitation. Photographs in the insets shows the colorimetric (bottom left) and luminescent (bottom right) responses of the chemodosimeter **1** (1.40×10^{-4} M): (1) **1** + CN^-; (2−9) **1** + SO_4^{2-}, HCO_3^-, HPO_4^{2-}, N_3^-, CH_3COO^-, NCS^-, NO_3^-, and Cl^-, respectively; (10) complex **1** alone.

at pH 7.4.[6] Such performance is highly comparable to other molecular sensors and dosimeters for CN^- in the literature.[5]

Specificity of Chemodosimeter 1. The specificity of **1** to CN^- over other anions can be explained by the relative stability of the donor−acceptor complex to that of adducts formed between the acceptor metal center and the analytes. As demonstrated in other chemosensing ensembles, the relative stability of the ensembles is important to the analyte-specificity in chemosensing.[3f,g] Table 3 shows the estimated Gibbs free energy change ($-\Delta G°$/kJ mol^{-1}) of the formation of the various Cu^{II}(dien)−anion adducts and Ru(II)−Cu(II) donor−acceptor complexes. Only Cu(dien)−CN^- exhibits a $-\Delta G°$ greater than that of **1**. This hints that the driving force for the cleavage of **1** by CN^- is the formation of the more stable Cu(II)−CN^- species. To examine this argument, chemodosimetric responses of an analogous donor−acceptor adduct, *cis*-$[Ru^{II}(bpy)_2(CN)_2]$−$[Cu(dien)]^{2+}$ (bpy = 2,2′-bipyridine) (**2**), was studied. The main difference between the two donor−acceptor adducts is that the Ru(II)−diimine donor in **1** possesses a net negative charge while that of **2** is neutral. The donor−acceptor binding strength of **2** is expected to be weaker than that of **1**. Luminescence responses of **2** to anions are observed at 634 nm. The blue-shift in the luminescence responses of **2** compared to **1** is also attributable to the difference in the Ru(II)−diimine chromophores involved. The *cis*-$[Ru(bpy)_2(CN)_2]$ chromophore in **2** possesses two less strongly σ-donating cyano ligands compared to the $[Ru(^tBubpy)(CN)_4]^{2-}$ chromophore in **1**. The relatively lower electron density on the Ru(II) center of **2** causes an increase in the energy of the ^{3}MLCT excited state and a blue-shift of luminescence responses. The $-\Delta G°$ of formation of adduct **2** is found to be 14.8 kJ mol^{-1}, which is lower than that of **1** (29.1 kJ mol^{-1}). Its stability is also lower than that of the Cu(II)−CN^-, Cu(II)−SO_4^{2-}, and Cu(II)−HCO_3^- adducts. Figure 5 shows the spectrofluoro-

Table 3. Comparison of the Binding Constants (log K_B) and the Gibbs Free Energy Changes ($-\Delta G°$) of the Chelation of Various Anions, $K_2[Ru(^tBubpy)(CN)_4]$, and *cis*-$[Ru(bpy)_2(CN)_2]$ by $[Cu(dien)(ClO_4)](ClO_4)$

acceptor	donor	log K_B[a]	$-\Delta G°$/ kJ mol^{-1}
$[Cu(dien)(ClO_4)](ClO_4)$	CN^-	6.64	37.9
$[Cu(dien)(ClO_4)](ClO_4)$	$K_2[Ru(^tBubpy)(CN)_4]$ (**1**)[b]	5.10	29.1
$[Cu(dien)(ClO_4)](ClO_4)$	SO_4^{2-}	4.67	26.6
$[Cu(dien)(ClO_4)](ClO_4)$	HCO_3^-	3.72	21.2
$[Cu(dien)(ClO_4)](ClO_4)$	*cis*-$[Ru(bpy)_2(CN)_2]$ (**2**)[b]	2.60	14.8
$[Cu(dien)(ClO_4)](ClO_4)$	HPO_4^{2-}	2.26	12.9
$[Cu(dien)(ClO_4)](ClO_4)$	N_3^-	1.77	10.1
$[Cu(dien)(ClO_4)](ClO_4)$	CH_3COO^-	1.72	9.8
$[Cu(dien)(ClO_4)](ClO_4)$	NCS^-	1.20	6.8
$[Cu(dien)(ClO_4)](ClO_4)$	NO_3^-[c]	0.35	2.0
$[Cu(dien)(ClO_4)](ClO_4)$	Cl^-[c]	0.35	2.0

[a] Unless otherwise stated, donor−acceptor binding strengths were measured by spectroscopic titration in 1:1 DMF−HEPES aqueous buffer, pH 7.4, and 0.01 M ionic strength at 25 °C. [b] Donor−acceptor binding strengths were determined by spectrofluorometric titration in 1:1 DMF−HEPES aqueous buffer, pH 7.4, and 0.01 M ionic strength at 25 °C. [c] The binding constants were obtained from the SC-Database reference.

---

(19) Bignozzi, C. A.; Chiorboli, C.; Indelli, M. T.; Rampi-Scandola, M. A.; Varani, G.; Scandola, F. *J. Am. Chem. Soc.* **1986**, *108*, 210.

(20) (a) Peterson, S. H.; Demas, J. N. *J. Am. Chem. Soc.* **1976**, *98*, 7880. (b) Peterson, S. H.; Demas, J. N. *J. Am. Chem. Soc.* **1979**, *101*, 6571.

(21) Shriver, D. F.; Posner, J. *J. Am. Chem. Soc.* **1966**, *88*, 1672.

(22) Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759.

(23) (a) Bartocci, C.; Bignozzi, C. A.; Scandola, F.; Rumin, R.; Courtot, P. *Inorg. Chim Acta* **1983**, *76*, L119. (b) Bignozzi, C. A.; Scandola, F. *Inorg. Chem.* **1984**, *23*, 1540.

(24) Demas, J. N.; Addington, J. W. *J. Am. Chem. Soc.* **1974**, *96*, 3663.

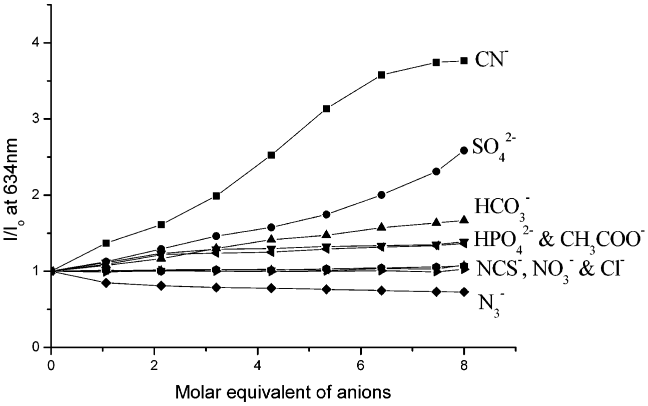


Figure 5. Summary of UV spectrofluorometric (top right) titrations of **2** (4.0×10^{-3} M) to common anions monitored as a function of the increase in emission (I/I_O at 634 nm). All titrations were carried out in aqueous DMF (1:1 v/v) at pH 7 at 298 K.

metric titrations of **2** with the various anions, and CN$^-$, SO$_4^{2-}$, and HCO$_3^-$ are found to be able to switch on, cleave the ensemble, and produce the luminescent response.

Conclusion

A new heterobimetallic Ru(II)−Cu(II) donor−acceptor complex **1** has been synthesized and characterized. This demonstrates that, with a suitable choice of metal centers and coordination ligands, heterobimetallic donor−acceptor complexes can be fine-tuned to produce sensitive chemodosimetric responses to specific analytes.

Acknowledgment. The work described in this paper was funded by a grant from the Research Grants Council of Hong Kong SAR, China (CityU 1108/02P), and a grant from CityU (Project 7001281).

Supporting Information Available: Crystallographic data (CIF format) and details of the IR and ESI-MS spectra of **1**, spectroscopic titrations between *cis*-[Ru(bpy)$_2$(CN)$_2$] and [Cu(dien)](ClO$_4$)$_2$ for the formation of **2**, electrospray mass spectra of **1** + NaCN, and details of spectrofluorometric titrations of **1** by CN$^-$ and other common anions (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC0492587